Doubly Ortho-linked Quinoxaline/Triarylamine Hybrid as a Bifunctional, Dipolar Electroluminescent Template for Optoelectronic Applications

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Experimental details of compounds 2a-c, 2c' and 3a,b, UV-Vis, PL, CV spectra, I-V-L characteristics and EL spectra of devices, ORTEP drawings and selected crystal data for 2c, 3a, and 3b (12 pages)

General.

1H NMR and 13C NMR spectra were recorded on Bruker AV500 (500 MHz 1H, 125 MHz 13C), Jeol JVM-EX400 (400 MHz 1H, 100 MHz 13C) or Varian Gemini-2000 (200 MHz 1H, 50 MHz 13C) spectrometers in deuterochloroform with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm (δ). Coupling constants, J, are reported in Hz. Infrared spectra were recorded on a Perkin-Elmer Paragon-500 FTIR spectrometer. Peaks are reported in units of cm⁻¹ with the following relative intensities: br (broad), s (strong 67-100 %), m (medium 33-67 %), or w (weak 0-33 %). Mass spectra were recorded on a Finnigan TCQ-700 spectrometer with an ionization voltage of 70 or 20 eV unless otherwise stated. High-resolution mass spectra were measured on JEOL SX-102A spectrometer. Combustion analyses were performed on a Perkin-Elmer 2400-CHN analyzer by the Northern Instrument Center of Taiwan. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT-95S spectrometer. Data are reported in the form m/e (intensity relative to base peak). Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light or with phosphomolybdic acid (PMA) and KMnO₄ staining agents. Column (flash) chromatography was performed using 32-63 µm silica gel. Solvents for extraction and chromatography were reagent grade. Dichloromethane was dried over CaH₂ before use. THF was dried over Na with benzophenone-ketyl intermediate as indicator. All reactions were run under argon. Absorption spectra (CH₂Cl₂) were measured on a HP-8453 Diode Array spectrometer using spectrophotometric grade solvents. Emission spectra (10 µM) were measured on an Aminco-Bowman Series 2 luminescence spectrometer upon excitation at
the absorption maxima in the same solvent. Quantum yield measurements were performed by using Coumarin-1 \(^1\) (99%, EtOAc) and DCM \(^2\) (65%, CH\(_3\)CN) as standards. X-ray structures were measured on Nonius CAD4 or Bruker Nonius Kappa CCD instrument. Cyclic voltammetry (CV) measurements were carried out in 1.0 mM of substrate in anhydrous degassed solvents containing 0.1 M tetrabutylammonium perchlorate (\(n\)-Bu\(_4\)NClO\(_4\)) as a supporting electrolyte on a PARC EG&G 273 potentiostat. Platinum electrode was used as a counter electrode and carbon electrode was used as a working electrode and Ag/AgCl as a reference electrode. Differential scanning calorimetry (DSC) analyses were performed on a TA Instrument DSC-2920 Low-Temperature Difference Scanning Calorimeter. The samples were firstly heated (20 °C/min) to melt and then quenched with liquid nitrogen. \(T_g\)s were recorded by heating (10 °C/min) the cooled samples.

**10,11-Dihydro-5H-dibenzo[b,f]azepine-10,11-diol\(^3\)**

A mixture of iminostilbene (5.01 g, 25.9 mmol), 4-methylmorpholine \(N\)-oxide (7.53 g, 55.6 mmol, 2.2 equiv), 1,4-diazabicyclo-[2,2,2]octane (DABCO, 0.3 g, 2.7 mmol, 0.1 equiv) and potassium osmate (0.010 g, 0.027 mmol, 0.1 mol%) was stirred in 50% aqueous acetone (100 mL) at ambient temperature for 24h. After completion of the reaction as evidenced by TLC analysis, the resulting reaction mixture was quenched with saturated aqueous Na\(_2\)SO\(_3\) (30 mL) and stirred for 30 min. The clear solution was concentrated under reduced pressure. The crude product was extracted with CH\(_2\)Cl\(_2\) (3 × 100 mL). The combined organic extracts were washed with water (30 mL), brine (30 mL), dried (MgSO\(_4\)), and evaporated to give 5.42 g (92 %) of the corresponding \(cis\)-diol as a colorless puffy material which was used directly for next step.

**11-Hydroxy-5,11-dihydro-dibenzo[b,f]azepin-10-one**

To a solution of diol (10.0 g, 44.0 mmol) in 1,4-dioxane (150 mL) at 15 °C was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 11.0 g, 48.5 mmol, 1.1 equiv) in portions. The resulting mixture was stirred at this temperature for 10 h.
After completion of the reaction as evidenced by TLC analysis, the reaction mixture was filtered and the filtrate was concentrated. The residue was re-dissolved in CH$_2$Cl$_2$ (50 mL) and the mixture was filtered again. Evaporation of the filtrate gave crude $\alpha$-hydroxy-ketone, which was re-crystallized from CH$_2$Cl$_2$ to provide 8.42 g (85 %) of the pure $\alpha$-hydroxy-ketone as colorless needles.

5H-Dibenzo[b,f]azepine-10,11-dione$^4$

A mixture of $\alpha$-hydroxy-ketone (2.7 g, 12.0 mmol), NH$_4$NO$_3$ (0.96 g, 12.0 mmol, 1equiv) and Cu(OAc)$_2$ (0.12 g, 0.6 mmol, 5 mol%) was heated in 80% aqueous AcOH (40 mL) at 80 °C for 30 min. The reaction mixture was gradually cooled to ambient temperature and then extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic layers were washed with water (30 mL), brine (30 mL), dried (MgSO$_4$), and evaporated. Purification of the crude residue by column chromatography on silica gel gave diketone as yellow solid, which was further re-crystallized from CH$_2$Cl$_2$ to give 1.472 g (55 %) of the pure product as orange needles: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.40 (s, 1H), 8.61 (d, $J$ = 8.8, 2H), 8.21 (d, $J$ = 8.8, 2H), 7.75 (dd, $J$ = 8.8, 6.8, 2H), 7.60 (dd, $J$ = 8.8, 6.8, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.4, 149.0, 132.1, 130.3, 129.9, 128.6, 123.5; TLC $R_f$ 0.37 (EtOAc/hexane, 1/7).

A solution of the diketone (4.0 g, 17.9 mmol), o-phenylenediamine (2.7 g, 25.1 mmol, 1.4 equiv) and catalytic amount of $p$-toluenesulfonic acid ($p$-TSA, 17 mg, 0.9 mmol, 5 mol%) in CHCl$_3$ (50 mL) was heated to reflux for 10 h. The reaction mixture was cooled to ambient temperature and then quenched with saturated aqueous NaHCO$_3$ (35 mL). The aqueous layer was separated and extracted with CH$_2$Cl$_2$ (2 ×100 mL). The combined organic layers were washed with water (35 mL), brine (30 mL), dried (MgSO$_4$), and evaporated. Purification of the crude residue by column chromatography on silica gel gave crude product, which was re-crystallized from CH$_2$Cl$_2$ to provide 4.49 g (85 %) of pure 2a as yellow needles: m.p. 211 °C (CH$_2$Cl$_2$, by DSC); $T_d$ 256 °C; $T_g$ 57 °C; IR (KBr) $\nu$ 3306 (w), 3059 (w), 1610 (m), 1596 (w), 1516 (m), 1477 (s), 1451 (m), 1365 (m), 1311 (m), 1246 (w), 1221 (w), 1141 (w); $^1$H
NMR (200 MHz, CDCl₃) δ 8.18-8.09 (m, 4H), 7.73 (dd, J = 6.4, 3.4, 2H), 7.38-7.18 (m, 4H), 6.92 (d, J = 7.8, 2H), 5.47 (s, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 152.6, 150.7, 141.7, 132.0, 130.8, 129.8, 129.7, 129.3, 124.2, 119.8; MS (20 eV) 295 (M⁺, 100), 75 (39), 62 (14), 52 (18), 50 (48); TLC Rf 0.35 (EtOAc/hexane, 1/8); HR-MS calcd for C₂₀H₁₃N₃: 295.1109, found: 295.1109; Anal. Calcd for C₂₀H₁₃N₃: C, 81.34, H, 4.44, N, 14.23. Found: C, 81.22, H, 4.59, N, 14.03.

Representative procedure for the preparation of 2b-c, 2c’, and 3a,b

To a solution of Q-H-2a (295 mg, 1.0 mmol), t-BuONa (288 mg, 3.0 mmol), Pd₂(dba)₃ (11.6 mg, 1 mol%) in dry toluene (15 mL) was added P(t-Bu)₃ (0.03 M in toluene, 1 mL, 3 mol%) and iodobenzene (224 mg, 1.1 mmol, 1.1 equiv). The resulting mixture was refluxed for 8h in argon atmosphere until complete consumption of 2a as evidenced by TLC analysis. The reaction mixture was then cooled to ambient temperature and quenched with saturated aqueous NaHCO₃ (20 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 25 mL). The combined organic extracts were washed sequentially with water (15 mL) and brine (10 mL), dried (MgSO₄), and concentrated to give crude product-2b, which was purified by column chromatography on silica gel (EtOAc/hexane, 1/10) afford the pure compound-2b in 87% yield as yellow solid: m.p. 213-214 °C (CH₂Cl₂/hexane, by DSC); Td 273 °C; Tg 86 °C; IR (KBr) ν 3066 (w), 1591 (m), 1498 (s), 1452 (m), 1350 (m), 1317 (m), 1283 (w), 1062 (w), 1020 (w); ¹H NMR (400 MHz, CDCl₃) δ8.22 (dd, J = 7.8, 1.2, 2H), 8.18 (dd, J = 6.4, 3.4, 2H), 7.78 (d, J = 6.4, 3.4, 2H), 7.65 (dd, J = 7.8, 1.6, 2H), 7.62 (td, J =
7.8, 1.4, 2H), 7.53 (td, J = 7.8, 1.6, 2H), 6.96 (dd, J = 8.8, 7.4, 2H), 6.60 (t, J = 7.4, 1H), 6.58 (d, J = 8.8, 2H); 13C NMR (100 MHz, CDCl3) δ 150.9, 147.4, 146.5, 141.5, 137.4, 132.6, 131.2, 130.1, 129.3, 129.1, 128.8, 127.8, 118.2, 112.0; MS (70 eV) 371 (M⁺, 100), 268 (10), 255 (20), 185 (10), 77 (10); TLC Rf 0.37 (EtOAc/hexane, 1/10); HR-MS calcd for C26H17N3: 371.1417, found: 371.1426; Anal. Calcd for C26H17N3: C, 84.07, H, 4.61, N, 11.31. Found: C, 83.86, H, 4.58, N, 11.20.

Data for 2c (yellowish solid): m.p. 273 °C (CH2Cl2, by DSC); Td 350 °C; Tg 154 °C; IR (KBr) ν 3054 (w), 1485 (m), 1449 (m), 1352 (m), 1312 (m), 788 (m), 754 (s), 741 (s), 730 (s); 1H NMR (400 MHz, CDCl3) δ 8.54 (s, 1H), 8.23-8.15 (m, 6H), 8.05 (d, J = 8.5, 2H), 7.80 (dd, J = 6.3, 3.4, 2H), 7.43 (t, J = 6.8, 2H), 7.31 (t, J = 8.0, 2H), 7.16 (t, J = 6.9, 2H), 7.09 (bd, J = 7.7, 2H), 7.03 (td, J = 6.8, 1.6, 2H); 13C NMR (50 MHz, CDCl3) δ 153.8, 152.0, 142.2, 136.7, 132.6, 132.4, 132.3, 131.4, 130.0, 129.9, 129.5, 129.0, 128.2, 126.8, 125.5, 124.3, 122.6; MS (70 eV) 471 (M⁺, 100), 293 (5), 234 (38), 190 (10); TLC Rf 0.4 (EtOAc/hexane, 1/9); HR-MS calcd for C34H21N3: 471.1735, found 471.1748; Anal. Calcd for C34H21N3: C, 86.60, H, 4.49, N, 8.91. Found: C, 86.48, H, 4.42, N, 8.92.

Data for 2c' (yellowish solid): m.p. 324 °C (CH2Cl2, by DSC); Td 464 °C; Tg 159 °C; IR (KBr) ν 3054 (w), 1485 (m), 1449 (m), 1352 (m), 1312 (m), 788 (m), 754 (s), 741 (s), 730 (s); 1H NMR (400 MHz, CDCl3) δ 8.52 (s, 1H), 8.27 (d, J = 8.7, 2H), 8.10 (dd, J = 7.8, 3.0, 2H), 8.04 (d, J = 8.4, 2H), 7.89 (s, 2H), 7.88 (dd, J = 6.6, 2.3, 4H), 7.43 (t, J = 7.6, 2H), 7.36 (t, J = 7.6, 2H), 7.08-7.03 (m, 8H), 6.95 (t, J = 8.3, 2H), 3.88 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 159.2, 152.0, 151.6, 140.0, 138.9, 137.1, 133.0, 132.3, 132.0, 131.5, 131.0, 129.8, 129.6, 128.9, 128.0, 126.8, 125.6, 125.4, 124.0, 122.6, 113.5, 55.3; MS (70 eV) 683 (M⁺, 100), 342 (96), 190 (20), 176 (16); TLC Rf 0.3 (EtOAc/hexane, 1/12); Anal. Calcd for C48H33N3O2: C, 84.31, H, 4.86, N, 6.15. Found: C, 84.43, H, 4.80, N, 6.17.
Data for 3a (yellow solid): m.p. 448-449 °C (CHCl₃/hexane, by DSC); T_d 467 °C; T_g 202 °C; IR (KBr) ν 3051 (m), 1630 (m), 1493 (m), 1443 (s), 1367 (m), 1306 (s), 1253 (m), 1203 (m), 1159 (m); ¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, J = 7.7, 1.3, 4H), 8.15 (dd, J = 6.4, 3.4, 4H), 7.73 (dd, J = 6.5, 3.4, 4H), 7.63 (dd, J = 7.8, 1.3, 4H), 7.59 (td, J = 7.0, 1.6, 4H), 7.50 (td, J = 7.6, 1.6, 4H), 7.00 (d, J = 7.2, 4H), 6.56 (d, J = 8.8, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 150.9, 147.4, 146.5, 141.5, 137.4, 132.6, 131.2, 130.1, 129.3, 129.1, 128.8, 127.8, 118.2; 112.1; MS (70 eV) 740 (M⁺, 43), 447 (11), 370 (18), 294 (80), 255 (100), 152 (13), 76 (12); TLC R_f 0.31 (CHCl₃/hexane, 1/3); HR-MS calcd for C₅₂H₃₂N₆: 740.2683, found: 740.2685; Anal. Calcd for C₅₂H₃₂N₆: C, 84.30, H, 4.35, N, 11.34. Found: C, 84.22, H, 4.39, N, 11.34.

Data for 3b (yellowish orange solid): m.p. 393 °C (CHCl₃/hexane, by DSC); T_d 470 °C; T_g 294 °C; IR (KBr) ν 3461 (w), 3047 (w), 1599 (m), 1490 (m), 1470 (s), 1454 (s), 1349 (m), 1312 (m), 1281 (m), 761 (s); ¹H NMR (400 MHz, CDCl₃) δ 8.19-8.15 (m, 4H), 8.12-8.10 (m, 4H), 7.79-7.75 (m, 4H), 7.49-7.41 (m, 12H), 7.10 (d, J = 7.6, 4H), 7.00 (t, J = 7.6, 4H), 6.71 (bd, J = 7.2, 4H), 6.60 (d, J = 2.4, 2H), 6.53 (dd, J = 8.8, 2.4, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 150.6, 150.5, 146.6, 145.7, 145.4, 141.0, 136.5, 132.0, 130.8, 130.4, 129.7, 129.0, 127.8, 127.5, 127.0, 125.7, 118.7, 111.8, 110.3, 62.8; MS (20 eV) 904 (M⁺, 50), 611 (30), 452 (100), 294 (40); TLC R_f 0.65 (CHCl₃/hexane, 3/7); HR-MS calcd for C₆₅H₄₀N₆: 904.3309, found 904.3304; Anal. Calcd for C₆₅H₄₀N₆-CH₂Cl₂: C, 80.07, H, 4.28, N, 8.49. Found: C, 80.08, H, 4.35, N, 8.29.

Device fabrication

Pre-patterned ITO substrates with effective individual device area of 3.14 mm² were cleaned by sonication in a detergent solution for 3 min and then washed with large amount of doubly distilled water. Further sonication in deionized water and ethanol for 3 min respectively was done before blowing dry with a stream of nitrogen. The ITO substrates were then treated with oxygen plasma for
three minutes before loaded into the vacuum chamber. The organic layers were deposited thermally at a rate of ~0.2 nm/s under a pressure of ~2 x 10^{-5} torr in an Ulvac Cryogenic deposition system. The first kind of typical devices were constructed with 40 nm of BPAPF as the hole-transporting layer (HTL), 40 nm of Q family derivative as the electron-transporting layer (ETL) as well as emission layer. The second kind of typical devices were comprised of 40 nm Q family derivative as the HTL and 40nm Alq3 or TPBI as the ETL. An alloy of magnesium and silver (ca. 10:1, 50 nm) was deposited as the cathode, which was capped with 100 nm of silver. The current-voltage-luminance was measured in ambient with a Keithley 2400 Source meter and a Newport 1835C Optical meter equipped with 818ST silicon photodiode.

Fig. S1. UV overlays of Q-Ar 2a-c, 2c’ and Q-spacer-Q 3a,b series (all in CH2Cl2): (top) full spectra; (bottom) expanded plots.
Fig. S2. Emission overlays of Q-Ar 2a-c, 2c′ (CH₂Cl₂) and Q-spacer-Q 3a,b (toluene) series

Fig. S3. Cyclic voltammogram overlays for 2a-c, 2c′ (2c in THF) and 3a,b in CHCl₃
**Fig. S4** The current-voltage-luminance \((I-V-L)\) characteristics and electroluminescence spectra of devices in Table 2.
Fig. S5. Chem 3D presentations and ORTEP drawings for the X-ray crystal structures of 2c, 3a, and 3b (solvent molecules were removed for clarity for 3b).
**Fig. S6.** Diamond presentation of for the X-ray crystal structure of 3b with CH$_3$CN and 1,4-dioxane (C$_4$H$_8$O$_2$) trapped in crystal lattice.

**Selected crystal data for 2c, 3a, and 3b:**

(a) Crystal data for 2c: C$_{34}$H$_{21}$N$_3$, $M = 471.54$, orthorhombic, space group P 21 21 21, $a = 11.012(4)$, $b = 14.223(6)$, $c = 15.175(7)$ Å, $U = 2376.7(17)$ Å$^3$, $Z = 4$, $D_x = 1.318$ g cm$^{-3}$, $\mu = 0.078$ mm$^{-1}$, $F(000) = 984.0$, $T = 293$ K, wavelength 0.70930 Å, crystal size $0.65 \times 0.55 \times 0.35$ mm, $\theta_{\text{max}} = 24.92^\circ$, 25013 reflections measured, final $R[I > 2\sigma(I)] = 0.0389$, CCDC 271946;

(b) Crystal for 3a: C$_{52}$H$_{32}$N$_6$, $M = 740.84$, triclinic, space group P -1, $a = 8.654(4)$, $b = 8.868(5)$, $c = 14.316(9)$ Å, $\alpha = 86.745(3)^\circ$, $\beta = 82.838(3)^\circ$, $\gamma = 61.349(3)^\circ$, $U = 956.61(9)$ Å$^3$, $Z = 1$, $D_x = 1.286$ g cm$^{-3}$, $\mu = 0.077$ mm$^{-1}$, $F(000) = 386.0$, $T = 295$ K, wavelength 0.71073 Å, crystal size $0.40 \times 0.20 \times 0.15$ mm, $\theta_{\text{max}} = 25.03^\circ$, 13258 reflections measured, final $R[I > 2\sigma(I)] = 0.0602$, CCDC 271944;

(c) Crystal data for 3b: C$_{71}$H$_{51}$N$_7$O$_2$, $M = 1034.22$, monoclinic, space group P 21/c, $a = 10.655(2)$, $b = 23.169(4)$, $c = 24.861(4)$ Å, $U = 6128.9(16)$ Å$^3$, $Z = 4$, $D_x = 1.121$ g cm$^{-3}$, $\mu = 0.070$ mm$^{-1}$, $F(000) = 2168.0$, $T = 293$ K, wavelength 0.70930 Å, crystal size $0.40 \times 0.10 \times 0.10$ mm, $\theta_{\text{max}} = 25.00^\circ$, 32085 reflections measured, final $R[I > 2\sigma(I)] = 0.0920$, CCDC 271945.

